

**CO adsorption on metal surfaces:
a hybrid functional study with plane wave basis set.**

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Abstract

We present a detailed study of the adsorption of CO on Cu, Rh, and Pt (111) surfaces in top and hollow sites. The study has been performed using the local density approximation, the gradient corrected functional PBE, and the hybrid Hartree-Fock density functionals PBE0 and HSE03 within the framework of generalized Kohn-Sham density functional theory using a plane-wave basis set. As expected, the LDA and GGA functionals show a tendency to favor the hollow sites, at variance with experimental findings that give the top site as the most stable adsorption site. The PBE0 and HSE03 functionals reduce this tendency. In fact, they predict the correct adsorption site for Cu and Rh but fail for Pt. But even in this case, the hybrid functional destabilizes the hollow site by 50 meV compared to the PBE functional. The results of the total energy calculations are presented along with an analysis of the projected density of states.

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I. INTRODUCTION

The adsorption of carbon monoxide on metal surfaces is an important case study in surface science for two reasons. On one hand, the interaction of CO with metal surfaces plays a major role in understanding phenomena related to e.g. catalysis, adhesion and coating as well as in many industrial processes, such as automotive catalysis, corrosion, tribology, and gas sensing.¹ Catalysts containing transition metals, such as rhodium, palladium and platinum have been widely used to lower the emissions of CO in automobile exhausts.¹ For all the mentioned applications, it is clear that understanding adsorption on both bare and adsorbate-covered surfaces is an important issue.

On the other hand, the failure of Density Functional Theory (DFT) based on local and semilocal density functionals in predicting the correct adsorption site for CO on metal surfaces is well known. The most notable example in literature is the CO/Pt(111) system, often referred to as *CO adsorption puzzle*. No "stone was left unturned"² in order to determine the reason for the discrepancy between theory and experiment, but neither defect structures and contaminations, nor relativistic or spin effects, nor zero-point energies can account for the difference: there is strong evidence that current approximations to DFT underestimate the CO preference for low-coordination sites.^{2,3} Most plane wave codes predict that the hollow site is preferred for CO on Cu, Rh and Pt (with the exception of Ref. 4 for CO on Rh), whereas experimentally it is found that CO adsorbs at the top site with the carbon end down at low coverage on all three substrates.^{5,6,7,8} In all fairness, it must be emphasized that some local basis set codes (specifically DMOL and ADF) seem to give the proper site order for Pt.^{9,10} The reason for the discrepancy between local basis set codes and plane wave codes is not yet entirely understood, but it is likely to be related to the different treatment of relativistic effects or basis sets. For Pt, the DMOL code for instance applies effective core potentials to take into account relativistic effects, and the site preference depends critically on the used effective core potential, with the most accurate effective core potential giving the same site preference as plane wave codes.¹¹ The Amsterdam Density Functional code (ADF) also yields the correct site order for Pt.¹⁰ Basis set convergence, k-point sampling as well as relativistic effects have been carefully checked for CO on Pt, and it is at this point unclear why results differ from those reported using plane waves.

Very recently, Q.-M. Hu *et al.*¹² have shown that errors of present-day exchange-

correlation (xc) functionals are rather localized and spatially limited to few nearest neighbors. For extended systems the *correction* can be estimated by analyzing properly chosen clusters and employing wavefunction based methods for an improved xc treatment. According to their study, this procedure applied to CO/Cu(111) and CO/Ag(111) gives the top site as the most stable adsorption site, in agreement with the experiments.¹² Returning to the discrepancy between theory and experiment obtained using DFT and plane waves, the current suggestion is that the main reason for the failure is due to the incorrect description of the relative position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of CO with respect to the Fermi energy of the metal.¹³ To overcome this problem several possibilities have been considered so far. One is to apply an a posteriori correction, based on the singlet-triplet CO excitation energy obtained by GGA and configuration interaction calculations.¹⁴ A second option is using a DFT+U approach, where an additional U is added to the DFT Hamiltonian to shift the CO LUMO to higher energies.^{3,15} A third self contained and less ad-hoc approach is the use of hybrid functionals.¹³

Hybrid functionals are a combination of exact non-local orbital-dependent Hartree-Fock (HF) exchange and a standard local exchange-correlation functional, and they provide a significant improvement over the LDA-GGA description for molecular as well as extended insulating and semiconducting solid state systems.¹⁶ For these systems, hybrid functionals are among the most accurate functionals available as far as energetics and structural properties are concerned.^{17,18,19}

Currently, the most popular ones are PBE0 (or PBE1PBE)^{20,21} and B3LYP^{22,23}. The former has been proposed by Perdew, Burke, Ernzerhof, Adamo and Barone^{24,25} as a "parameter-free" functional based on the PBE exchange-correlation functional. It has promising performance for all important properties, being competitive with the most reliable, empirically parametrized functionals.²¹ The latter was suggested by Becke²² and soon developed into the most popular and most widely used functional for quantum chemical calculations. This functional reproduces the thermochemical properties of atoms and molecules rather well.²⁶

For periodic systems, in particular metals, however, the long-range nature of the Fock exchange interaction and the resultant large computational requirements present a major drawback. Recently, a new hybrid functional, called HSE03, has been introduced by J. Heyd

*et al.*²⁷ This functional addresses this problem by separating the description of the exchange interaction into a short- and a long-range part, where the long-range part is treated by semilocal gradient corrected functionals. The new functional yields a description of molecular properties comparable to the results obtained using the PBE0 functional, and, in some cases, it even gives a slight improvement over the latter.²⁷

To the best of our knowledge, very few *ab initio* calculations based on hybrid functionals have been concerned with the problem of CO adsorption on metal surfaces. Gil *et al.*¹³ reported on the CO adsorption on the Pt(111) surface using both slabs and cluster models with local, semilocal and hybrid functionals (B3LYP). But the B3LYP calculations were restricted to clusters and extrapolation to large clusters seems to indicate that convergence with respect to the cluster size was not obtained. The B3LYP functional renders the on top and fcc sites almost degenerate, whereas LDA and GGA show a pronounced tendency to favour fcc adsorption. This was confirmed in the work of Doll²⁸ on the same system, where a careful comparison between gradient corrected functionals and the B3LYP functional has been reported. It was shown that the B3LYP functional gives the top site as the preferred site. Finally, in the work of Neef and Doll,²⁹ the adsorption of CO on the Cu(111) surface has been studied using the local density approximation, the gradient corrected functional of Perdew and Wang and the B3LYP functional. The LDA and GGA yield the fcc site as favorable adsorption site, whereas the B3LYP functional results in the preference of the top site, in agreement with the experiment. The recent study for CO on Cu and Ag(111) come to similar conclusions.¹² All these hybrid functional studies applied only B3LYP and they made use of localized basis sets, which are possibly affected by basis set superposition errors (BSSE).

The aim of the present report is to present an extensive density functional study of the adsorption of CO on close-packed (111) metallic surfaces using the PBE0 and HSE03 functionals, which have not been considered yet for this specific problem. We also include, for comparison, the local density approximation and the standard gradient corrected PBE functional, which is widely accepted as the best parameter-free density functional available. We discuss in detail the application of these functionals to bulk, bare Cu, Rh and Pt surfaces and the corresponding CO adsorption problem.

The study is pursued within the framework of the plane-wave projector-augmented-wave (PAW) formalism. Based on the approach of Chawla and Voth³⁰ for the evaluation of the

exact exchange, PBE0 and HSE03 functionals have been recently implemented in the Vienna ab-initio Simulation Package (VASP).³¹ We remark that the use of a plane-wave basis set for the evaluation of the exact exchange energy allows for calculations that are free of basis-set superposition errors and benefit from the computational efficiency of fast Fourier transforms. Details of the implementation are given elsewhere.^{16,32} We will focus on three reference metal systems, Cu, Rh, and Pt, which are among the best studied metallic surfaces concerning CO adsorption.¹ We note that the adsorption of CO on Rh(111) has not been investigated using hybrid functionals.

The paper is organized as follows. In the next Section we describe the computational approach and the model systems used; in Sect. III we briefly review the calculated properties for the bulk and corresponding bare (111) surfaces as well as for the CO molecule; in Sect. IV we discuss the results concerning the structural properties and energetics of the adsorbed CO molecule on the surface; Sect. V is devoted to the electronic properties in terms of density of states; in Sect. VI we discuss the main results of this work and in Sect. VII we draw our conclusions.

II. THEORETICAL AND COMPUTATIONAL METHOD

The first principles density functional theory calculations have been performed within the local and generalized gradient density approximation to DFT in the Ceperley-Alder and Perdew-Burke-Ernzerhof parametrization, respectively.^{33,34} In the present calculations, the interaction between the ions and valence electrons is described by the projector augmented wave (PAW)³⁵ method in the implementation of Kresse and Joubert.³⁶

The cutoff energy has been fixed to 400 eV, which is sufficient to give well converged results for the systems considered in this work.³² The surfaces have been modelled by a periodic four layer metal slab with a CO molecule adsorbed on one side of the slab, vertical to the (111) surface plane (asymmetric setup). For CO on Pt(111), tests with a six layer metal slab using the HSE03 functional have also been performed in order to check the convergence with respect to the slab thickness: the relative stability of the different sites does not change. Each slab is separated from its periodic image in the z -direction by a vacuum space of ~ 10 Å. The two uppermost surface layers and the CO molecule are allowed to relax (substrate buckling up to the second layer below the surface). For the electronic

relaxation, we fix the energy threshold to 10^{-3} eV whereas, the ionic relaxation is stopped when all forces are smaller than 0.1 eV/Å. We use a $c(2 \times 4)$ in-plane periodicity, which is equivalent to a coverage of $\Theta = 0.25$ ML. With this choice, the separation between the molecule and its in-plane periodic images is large enough to neglect spurious adsorbate-adsorbate interactions with a reasonable computational effort.³⁷

For the HSE03 calculations, the range separation parameter ω was set to $\omega = 0.3 \text{ Å}^{-1}$ in both the density functional part as well as the non-local Fock exchange.³⁸

The Brillouin zone integrations are performed on symmetry reduced grids using the Monkhorst-Pack scheme.³⁹ To accelerate k-point convergence, we set the Methfessel-Paxton⁴⁰ smearing width to 0.1 eV. We have carefully checked the k-point convergence by performing calculations using $4 \times 4 \times 1$, $6 \times 6 \times 1$ and $8 \times 8 \times 1$ points (see discussion in Sect. IV). The numerical accuracy of the adsorption energies is estimated to be ~ 20 meV. We have also investigated the effect of downsampling the reciprocal space representation of the Fock exchange operator for the HSE03 functional as outlined in Ref. 32. In particular, the Fock exchange operator has been evaluated on the "full" $n \times n \times 1$ k-point mesh, as well as, on the corresponding "downsampled" $\frac{n}{2} \times \frac{n}{2} \times 1$ grid, with $n=4, 6, 8$ (for details see Ref. 32). Results are discussed in Sect. IV. Finally, we have also tested, for a reference case (HSE03), the effect of the parameter that controls the fast Fourier transformation (FFT) grid for the HF routines (keyword ENCUTFOCK in the VASP code). By considering the smallest possible FFT grid that just encloses the cutoff sphere corresponding to the plane wave cutoff (ENCUTFOCK=0) or simply removing this constraint (without the flag ENCUTFOCK), total energies change by less than 5 meV.⁴¹

We considered three adsorption sites: top site, where CO is sitting vertically above a metal atom in the top layer, and the hcp (fcc) hollow site, where CO is sitting vertically above a metal atom in the second (third) topmost layer.

III. BULK, BARE SURFACE AND CO MOLECULE

Before studying the effect of CO adsorption on the (111) metal surfaces, we first consider the bulk and bare surfaces. In Table I we summarize the results for the bulk systems reporting the lattice constant (a_0) and the bulk modulus (B_0) obtained using the Murnaghan equation of state. The cohesive energy (E_{coh}) is calculated considering unconstrained, i.e.

spin polarized and nonspherical, ground states of the atoms.¹⁶ The numbers between round brackets give the relative errors with respect to experiment.

As usual, the LDA (GGA) lattice constants are slightly underestimated (overestimated) with respect to the experiment. Note that the experimental lattice constants reported in Tab. I have not been extrapolated to 0 K and the zero-point quantum fluctuations have not been included in the DFT calculations. However, the inclusion of these contributions should change the values by only approximately ~ 0.1 %, which we can neglect for the purpose of the present study.⁴²

Using hybrid functionals, the lattice constant is almost unchanged for Cu (only a slight expansion is found using PBE0 and HSE03) and the overestimation is generally reduced in the other two cases. For Rh, the hybrid functionals overcorrect the lattice constant giving a theoretical value smaller than the experimental one; for Pt, it remains slightly larger than experiments. Except for Cu, the agreement with experiment improves using hybrid functionals (the PBE0 and HSE03 relative errors are smaller than the PBE ones).

The overestimation (underestimation) of the lattice constants goes in hand with an underestimation (overestimation) of the bulk-moduli. The PBE functional predicts B_0 slightly more accurately than hybrid functionals for the systems under study.

The cohesive energies are overestimated at the LDA level, they are very well reproduced for the three bulk metals at the PBE level, but they are underestimated using hybrid functionals. The underbinding has been attributed to the admixture of Fock exchange, and to the fact that Hartree-Fock usually underbinds, especially for metals.^{28,43} We believe that this is not generally true for hybrid functionals. In fact, as shown in Ref. 32, the atomization energies for systems without d electrons, like Li, Na and Al are quite comparable for the PBE, PBE0 and HSE03 functionals (and very close to experimental results within 0.05-0.15 eV). Most probably, the reason for the reduction of the atomization energies of d metals is related to the increased stability of the spin polarized atom compared with an artificial non-spin-polarized atom. The hybrid functional overestimates the exchange splitting in d elements, with a consequent increase of the spin-polarization energy. This however does not explain the discrepancy for Cu. Here we believe that the neglect of dynamical correlation effects between closed d shells is a major source of errors accounting for roughly 210 meV of the discrepancy.⁴⁴ Proper inclusion of these Van der Waals-like forces would also decrease the theoretical lattice constant of Cu.

For Cu and Pt, we can compare our hybrid functional results with Ref. 28 and Ref. 29, respectively. From Tab. I, it is evident that our results are significantly closer to the experiment than those of Ref. 28 and Ref. 29 at the bulk level. This is most likely related to the B3LYP functional being specifically designed for small molecules, limiting or reducing its precision for heavy elements.⁴⁵

In Tab. II we show the relevant properties of the bare surfaces: d_{12} is the interlayer distance between the first and second topmost surface layer (and the corresponding relative variation with respect to the theoretical bulk value in round brackets) and the surface energies (E_{surf}).

For all functionals, the Cu and Rh surface layer relaxes inwards. For Pt, the top layer relaxes outward. This "anomalous" relaxation is already documented in literature.^{46,47} The change of d_{12} relative to the theoretical interlayer bulk distance (Δd_{12}) for Cu is -0.9% using PBE, in agreement with calculations of Neef (PW91); the same quantity calculated using PBE0 (HSE03) is -1.8% (-0.9%) which is again close to the one obtained using B3LYP in the same work (-1.2%). For Rh, Δd_{12} is -1.6% (PBE), -0.6% (PBE0), -1.0% (HSE03) and for Pt it is $+0.7\%$ (PBE), $+1.3\%$ (PBE0) and $+1.3\%$ (HSE03). Our values obtained both using standard GGA and hybrid functionals are slightly smaller than those obtained by Doll. The comparison with experiment is not simple due to the large uncertainties of the experimental values: for Cu Δd_{12} is $-1.0 \pm 0.4\%$,⁴⁸ for Rh it is $-1.3 \pm 0.9\%$,⁴⁹ and for Pt it is $+1.1 \pm 0.4\%$.⁴⁷ Agreement between our calculations and experimental results is certainly reasonable.

The calculated LDA surface energies compare well with previous calculations.⁵⁰ The GGA surface energy is 0.45, 0.81 and 0.62 eV, for Cu, Rh and Pt, respectively, also in agreement with the values reported in the literature (0.50 eV, 0.81, 0.65).^{28,51,52} The PBE0 and HSE03 functionals give a slightly increased surface energy compared to the PBE functional. Such an increase of the surface energies is pointing towards an improved description using the hybrid functionals, but they are still underestimated compared to experiments: the experimental surface energies are ~ 0.65 eV for Cu(111), ~ 1.08 eV for Rh(111), ~ 1.08 for Pt.⁵³ The B3LYP results^{28,29} do not follow a consistent trend, with an increased surface energy for Cu and a decreased one for Pt. We have also calculated the PBE and HSE03 work function for the three (111) metal surfaces (not shown in Tab. II). For Cu, we have 6.34 (6.10) eV; for Rh, 5.38 (5.05) eV; for Pt, 5.69 (5.64) eV using the PBE (HSE03) functional.

The experimental values are 4.98, 4.98, 5.65 eV for Cu, Rh and Pt.⁵⁴ We note that PBE values are overestimated compared to experimental values; the HSE03 functional reduces the overestimation and gives better agreement with experiments especially for Rh, and Pt.

Finally for the CO molecule, the calculated bond-length (d_{CO}) is 1.135, 1.143, 1.133, 1.131 Å for LDA, GGA (PBE), PBE0, HSE03, close to the values reported by Neef (1.150 and 1.140 Å using PW91 and B3LYP²⁹). The experimental bond length is 1.128 Å.⁵⁵ As far as the HOMO-LUMO gap is concerned we find 6.80, 6.90, 10.60, 8.80 eV using LDA, GGA (PBE), PBE0, and HSE03 respectively. The hybrid functionals give an energy gap increased by ~ 2 -3 eV due to the downshift of the HOMO and a simultaneous upshift of the LUMO. The negative of the calculated HOMO energy is 9.0, 8.6, 10.6, 10.0 eV using LDA, GGA (PBE), PBE0 and HSE03 respectively, compared to the experimental ionization potential of 14.10 eV.⁵⁶

IV. CO ADSORPTION: ENERGETICS AND STRUCTURAL PROPERTIES

In Table III, IV and V we show the results for the adsorption of a CO molecule on Cu, Rh and Pt surfaces, respectively. As expected, using the standard LDA and GGA functionals the wrong site is preferred (shown in boldface), namely fcc, hcp and fcc for Cu, Rh and Pt in agreement with previous calculations.^{28,29,57} The order of the sites with respect to the energy (starting from the most stable one) is fcc, hcp, top for Cu; hcp, fcc, top for Rh; fcc, hcp and top for Pt. These site orders generally agree with those reported in Refs. 28, 29 and 57, although different surface reconstructions and computational methods were used. It should be noted that, for the Cu case, our calculated adsorption energy for the most stable site is lower by more than 400 meV compared to that given in Ref. 29. Also the surface energy (bare surface) differs (see previous Section). These discrepancies can be possibly related to the different computational method used in Ref. 29, where a local basis set has been applied.

Using PBE0 or HSE03, the top site is preferred for Cu and Rh, in agreement with experiment. For Cu and PBE0 and HSE03, the site order is top, fcc, hcp (the same as found in Ref. 29 using B3LYP). The calculated adsorption energy (top site) is about -0.60 eV. This value is also close to that reported in Ref. 29 (-0.57 eV). The relative energy splitting (ΔE) between hcp and top is ~ 40 meV using PBE0 and ~ 30 meV using HSE03. A larger energy splitting (150 meV) was found by Neef,²⁹ and an even larger one (~ 200 meV) in

Ref. 12 using B3LYP. Furthermore, we find an almost degeneracy between the top and fcc sites using HSE03 ($\Delta E \approx 6$ meV).

For Rh, the site order is top, hcp and fcc using both hybrid functionals. The calculated adsorption energy is -2.109 and -2.012 eV using PBE0 and HSE03. The splitting top-fcc is only ~ 5 meV using PBE0 and ~ 16 meV using HSE03, hence certainly within the error bars of the present calculations. Therefore, even though the calculated adsorption energies predict the correct site order for Cu and Rh, we can only safely conclude that the applied hybrid functionals reduce the tendency of LDA and GGA functionals to favor the hollow site with respect to the top sites.

Finally, for Pt, neither PBE0 nor HSE03 recover the correct site preference: the top site remains unfavoured with respect to the fcc site, and the top and hcp sites are almost degenerate within the numerical accuracy. We, however, note that the top-fcc energy difference is ~ 350 meV (LDA), ~ 160 meV (GGA), ~ 56 meV (PBE0) and ~ 70 meV (HSE03). Therefore, the tendency to favour the hollow sites is again reduced using hybrid functionals, but not sufficiently so for Pt. In order to rule out possible errors due to the k-point mesh, we performed additional calculations for the HSE03 case and CO on Pt using a $12 \times 12 \times 1$ k-point grid and downsampling the HF exchange part to $6 \times 6 \times 1$ k-points. We found that the relative stability of the top and fcc sites changed by only ~ 20 meV. Also increasing the number of layers to 6 did not change the site order. The presented numbers are thus essentially converged.

Finally we compare the calculated adsorption energies of Cu, Rh and Pt with experimental values. For Cu(111), the experimental values are in the range of -0.52 to -0.46 eV,^{58,59} close to our calculated value (≈ -0.60 eV). For Rh(111), they are between -1.65 and -1.43 eV^{60,61}. In this case, the theoretical values are too large by ~ 0.40 - 0.60 eV and, worse, the hybrid functionals give a slight increase of the adsorption energy compared to the gradient corrected functional. This result is certainly disappointing, and we will return to it in the conclusions. For Pt(111), experimental values are in the range of -1.71 to -1.43 eV,^{62,63,64} which compare reasonably well with the PBE value. Again the hybrid functionals clearly worsen the agreement with experiment.

Concerning the geometry relaxations, we summarize the trend common to all the three functionals: i) the CO bond length is slightly elongated with respect to the theoretical value for the isolated molecule ($d_{\text{CO}} = 1.14$ Å) in the top site, and even more so in the hollow

sites. This holds for all three metal surfaces. ii) The elongation of d_{CO} correlates with a corresponding contraction of $d_{\text{C-X}}$ from low coordination (top) to high coordination sites (fcc, hcp). iii) The buckling b is larger for the top site. iv) Δd_{12} varies significantly from top to hcp sites, especially for Cu, where an inward relaxation for atop adsorption and an outward relaxation for the hollow sites is observed, whereas an outward relaxation is found in all three sites for Rh and Pt.

We conclude this section with a brief discussion of the k-point convergence presented in Tab.VI. Concentrating first on the PBE functional, we note that k-point convergence is slowest for the Cu surface, but fairly fast for the other two systems. A relative precision of 10 meV can be attained using $6 \times 6 \times 1$ k-points for all three systems [sampling specified for $c(2 \times 4)$ supercell]. The $4 \times 4 \times 1$ k-point set results in errors between 80 meV (Cu), 30 meV (Rh) and 10 meV (Pt). The HSE03 functional shows a similar convergence rate, with errors being only slightly larger. Now $6 \times 6 \times 1$ k-points are sufficient to yield energies to within a precision of 15 meV, whereas the $4 \times 4 \times 1$ k-point grid causes errors between 120 meV (Cu) and 30 meV (Rh and Pt). Reducing the k-point sampling for the presentation of the non-local Fock exchange part has only a very small effect on the relative energies (10 meV), which is more than acceptable, in particular, in view of a speed up by a factor four if the sampling for the non-local part of the Hamiltonian is reduced in x and y direction by a factor 2.

The PBE0 functional, however, converges exceedingly slowly, with discrepancies between $6 \times 6 \times 1$ and $8 \times 8 \times 1$ k-points being up to 50 meV. We were unable to increase the k-point grid beyond $8 \times 8 \times 1$ points with our available computational resources, but the relative energies using $8 \times 8 \times 1$ k-points are typically within 10-20 meV of those obtained using the HSE03 functional, and we expect them to come even closer to the HSE03 results, if the k-point set were further improved. This clearly demonstrates that the HSE03 functional is vastly superior in terms of computational requirements, in particular, for metallic systems. The calculations using the HSE03 functional and $6 \times 6 \times 1$ k-points with the Hartree-Fock part presented on a $3 \times 3 \times 1$ k-point grid are typically a factor 12 faster than the PBE0 calculations using $8 \times 8 \times 1$ k-points, although both yield practically the same results.

V. ELECTRONIC PROPERTIES

According to the Blyholder model⁶⁵ the interaction of the CO molecule with a transition metal surface is usually described as the sum of two contributions. The first is due to the overlap of the highest occupied molecular orbital (HOMO) 5σ with metal states. Since this interaction is accompanied by donation of electrons from the 5σ orbital into empty metal surface orbitals, this term is called donating term. The second term is due to the interaction of the surface-electron bands with the lowest unoccupied molecular orbitals (LUMO) $2\pi^*$. This is a back-donating term, since now electrons are transferred from the metal surface orbitals into the $2\pi^*$ orbitals. This simplistic model has been refined by A. Föhlisch,^{66,67} using x-ray emission spectroscopy and *ab initio* cluster calculations. They showed that the π bonding is manifested through the creation of a d_π complex related to a hybridization of 1π and $2\pi^*$ orbitals with metal states. The 4σ and 5σ orbitals and the metal states form a hybrid d_σ band. The work of Föhlisch concentrates mainly on the interaction of the frontier orbitals with metal d states, however, another often overlooked issue is that CO chemisorption to a transition-metal surface also involves interactions between the broad metal sp valence electron band (which contains approximately one electron per atom for Cu, Rh, Pt) and the CO orbitals. Due to symmetry, the $2\pi^*$ orbital can not interact with the s or p_z orbitals for top site adsorption, but the $2\pi^*-sp_z$ interaction is strong at high coordination sites, since *antisymmetric* combinations of surface s orbitals are available at these sites.⁶⁸

In order to gain insight on the effect of hybrid functionals on the electronic properties, we show the orbital resolved electronic density of states (DOS) for the Cu, Rh and Pt surfaces in Fig. 1, Fig. 2, and Fig. 3 respectively. For each Figure, we show the DOS for the bare surface layer [(a), panels d, sp], for CO adsorbed on the top [(b), panels d, sp, CO], and hollow site [(c), panels d, sp, CO] as obtained using PBE (left column) and HSE03 (right column). Here d, sp, CO indicate the projection onto d , sp metal states, and CO molecular orbitals respectively. In panel (a)-d, we show the one-electron energies of the 4σ , 1π , 5σ molecular levels aligned with the Fermi level using bold tick marks.⁶⁹

Since there are no principal differences between the PBE0 and HSE03 DOS, only results for the latter are shown. We caution the reader that the following analysis based on the atom-projected DOS can only give qualitative insight on variations of the chemisorption

energies upon changing the adsorption sites, the metal surface and the exchange-correlation functional. A more powerful and quantitative analysis can be done by using the concept of *surface group orbitals* introduced by R.A. van Santen,^{70,71,72} but this is beyond the purpose of this paper.

We recall the basic features of the interaction of the CO molecule with the metal surface,^{3,68,73,74} and we first focus on the PBE DOS for the Cu case (Fig. 1, left column). From panel (a)-d and (a)-sp, we note that the Cu d band is *almost* completely filled, it is centered around $\epsilon_d \sim -2.4$ eV (d band center of gravity) with $\delta\epsilon_d=1.52$ eV (d band width);⁷⁵ the sp band extends over a larger energy range below the Fermi energy, but it is strongly peaked around -5 eV; the 5σ level is located at ~ -2.70 eV, and the $2\pi^*$ level is positioned at ~ 4.20 eV above the Fermi energy.

Let us now consider the interaction of the metal states with the CO σ orbitals in the top configuration [Fig. 1 (b)]. The metal d bands broaden and shift down to lower energies due to the interaction with the CO molecule [compare panels (b)-d with (a)-d]. In particular, the d_{z^2} DOS is strongly modified. From panel (b)-CO we see that the 4σ and 5σ orbitals are shifted to lower energy (two main peaks at -10 and -7 eV with continuous line). Comparing panels in (b), it is clear that a strong interaction between d_{z^2} and sp_z metal states and the σ molecular states takes place giving rise to a bonding contribution below the Fermi level (below ~ -6 eV) and non-bonding and antibonding contributions partly even above the Fermi level (d_σ band).^{66,68} We recall that, since almost fully occupied states are interacting, the interaction would be only a Pauli-like repulsion, if the antibonding $\sigma - d_{z^2}$ hybrid states were not pushed above the Fermi level (relief of Pauli repulsion).⁷⁶ The corresponding depletion of 5σ states (donation from CO to the metal) is in accordance with the Blyholder model.

Let us now consider the π orbitals. From panel (b)-CO, we note that they are shifted to lower energy due to the interaction with d_{yz} , d_{xz} and sp metal states (bonding contribution). The 1π states are found at ~ -7 eV (dotted line), and a small peak of $2\pi^*$ symmetry at the position of the 1π orbital is visible and related to the $1\pi - 2\pi^*$ hybridization.⁶⁶ Above -6 eV, a non-bonding and antibonding 1π -derived band develops (d_π band)⁶⁶ which, however, remains below the Fermi energy (Pauli-like repulsion). The bonding states due to the interaction between the $2\pi^*$ orbital and the d band are found around -4 eV (again d_π complex)⁶⁶ and antibonding interactions well above the Fermi energy (not shown in the

Figure). The partial occupation of the $2\pi^*$ molecular orbital corresponds to a back-donation of electrons from the substrate to the originally empty $2\pi^*$ molecular orbital, in accordance with the Blyholder model.

For the hcp site, there are some differences. The d_{z^2} orbital is only marginally affected upon adsorption, whereas the d_{yz} (d_{xz}) and d_{xy} ($d_{x^2-y^2}$) bands are broadened and shifted to lower energy [compare panel (c)-d with (a)-d]. The interaction is mainly with the π orbitals: the peaks with dashed and dotted lines above -6 eV in panel (c)-CO have increased compared to the corresponding ones in panel (b)-CO. In accordance with the arguments of Ref. 68, the interaction between the metal s and p states and the CO π states is also enhanced, as reflected by a downshift of the metal sp states. Note that three metal atoms are affected by adsorption in the hollow site as compared to one metal atom for the atop site. In summary, the $\pi - d$ and $\pi - sp$ interaction is larger for the hcp site than for atop adsorption.

At this point, before considering the HSE03 DOS, we stress again that CO chemisorption to a transition-metal surface involves interaction of the molecular frontier orbitals and the broad s and narrow d band. The question whether the single-atom or high coordination site is favoured is clearly the result of a subtle balance between *single-atom* favouring interactions with the 5σ molecular states and *high-coordination* favouring interactions with the $2\pi^*$ molecular states. For CO on Cu(111) the balance between *single-atom* and *high-coordination* directing interactions is such that the hollow site adsorption is favoured for the PBE functional.

We now turn our attention to Fig. 1 right column. For the bare surface [(a)-d], we see that the d states are shifted to lower energy by ~ 1 eV with respect to the Fermi level compared to the PBE DOS ($\epsilon_d = -3.6$ eV), but the overall spectral shape and the bandwidth remain almost unchanged. The downward shift of the HSE03 d bands can be understood as a result of the reduction of the self-interaction (SIC) within the d shell in the hybrid-functional formalism. It is also clearly seen that the occupied (unoccupied) molecular levels are shifted downwards (upwards) with respect to the Fermi energy: the 5σ level is now located at -4.30 eV and the $2\pi^*$ level is at 4.50 eV. The change of the energy positions of the non-interacting molecular levels with respect to the Fermi energy is mainly related to the increased HOMO-LUMO gap in the free molecule, but also partly caused by the reduced work function for the HSE03 functional (6.10 eV compared to 6.30 eV for PBE). The effect of the inclusion

of part of the exact exchange on the broad sp band is different. As a matter of fact, the sp band is restrained to be located at the Fermi level (it is partially occupied), and the main effect of the non-local exchange is to increase the total bandwidth by 0.70 eV [compare left and right panel (a)- sp]. The above analysis immediately leads to a first conclusion. The down-shift of the d band and *simultaneous* up-shift of the $2\pi^*$ levels suggest a reduced $2\pi^*-d$ interaction: according to second order perturbation theory, the larger energy distance between the unperturbed energy levels weakens the interaction. Inspection of the calculated DOS confirms this conjecture for HSE03: i) the d_π peaks are much weaker, ii) hybridization between $2\pi^*$ and 1π molecular orbitals decreases corresponding to a *decrease* of the bonding interaction between the CO π -states and the metal d states according to Föhlisch.⁶⁶

We now summarize our analysis concerning the differences between the PBE and HSE03 functional. For the non-interacting fragments (bare surface and CO molecule) the HSE03 functional i) pushes the occupied molecular levels down in energy, whereas the unoccupied molecular orbitals are moved up in energy, and ii) the fully occupied d band is shifted down in energy. We have seen that these two *combined* effects generally disfavour the $\pi - metal$ interaction. It decreases for both the atop and the hollow site, but the destabilization is stronger in the hollow sites, in accordance with the observation that the $2\pi^*$ interaction is dominant at the hollow sites. This is confirmed by the observation that the adsorption energies in Tab. III decrease for both atop and hollow sites, but the effect is twice as strong for the hollow sites (compare the relative variation of the adsorption energies from PBE to HSE03, in Tab. III). A quantitative confirmation of this picture stems from the occupation of the $2\pi^*$ orbital in the hollow site. We recall that the larger the $2\pi^*$ occupation is, the stronger is the interaction of $2\pi^*$ with the metal states.⁶⁸ The $2\pi^*$ occupation is 0.80 and 0.66 electrons using PBE and HSE03 respectively, hence the occupation decreases by $\sim 17\%$ from PBE to HSE03.

Let us now consider the CO adsorbed on the Rh(111) surface in Fig. 2. In the following, we mainly concentrate on the differences between the PBE and HSE03 description (left and right panels). For the bare surface and HSE03 [panel (a)-d], there is a general downshift (upshift) of the occupied (unoccupied) part of the d bands with respect to the Fermi energy. This leads to a small downshift of the center of gravity ($\epsilon_d = -1.86$ and -2.23 eV using PBE and HSE03) and a sizeable larger bandwidth ($\delta\epsilon_d = 7.40$ and 8.90 eV using the PBE and HSE03 functional). For atop adsorption [panel (b)-d], we see a small decrease of the

intensity of the corresponding d_π band [dotted line in panel (b)-CO]. There is also a small reduction of the 1π and $2\pi^*$ hybridization and of the $2\pi^* - d$ interaction (reduction of the intensity of the corresponding broad bands with dashed line). As far as the $\sigma - d$ interaction is concerned, one can see from panel (b)-CO that the d_σ band is slightly less intense at the HSE03 level (reduction of the interaction strength). For the hcp site, we observe the same trends as for the top site.

Let us summarize again the differences between PBE and HSE03. As opposed to Cu, the d band is only slightly shifted downwards, but possesses a much larger bandwidth (1.50 eV). As a result, the strength of the $\pi - d$ interaction is only slightly reduced using HSE03: the reduction of the $\pi - d$ interaction caused by the up-shift of the $2\pi^*$ orbital is counteracted by the larger d bandwidth of the metal using HSE03. This is corroborated by the $2\pi^*$ occupation for the hollow site, which changes only from 1.05 to 1.01 electrons (*i.e.* $\sim 4\%$) going from PBE to HSE03. We recall that for Copper, the variation was about 17 %, *i.e.* much larger than for Rh. Secondly, the s electrons are largely affected by the introduction of the non-local exchange. For the bare surface, HSE03 reduces the self-interaction within the s shell and moves them to lower energies. This suggests an enhancement of the back-donation due to the interaction of the $2\pi^*$ states with antisymmetric linear combinations of metal s orbitals, which, we recall, is active only for the hollow site.⁶⁸ For Rh, the balance between atop- and hollow-directing interactions gives still a slight preference for atop adsorption using HSE03 (cfr. Tab. III).

Finally we turn our attention to Pt(111). Basically we observe the same trends as for Rh using HSE03, a down-shift of the d band center of gravity and a larger bandwidth is observed ($\epsilon_d = -2.13$ and -2.53 eV, $\delta\epsilon_d = 8.29$ and 9.32 eV using PBE and HSE03, respectively). The work-function changes only a little (5.69 and 5.64 using PBE and HSE03). For both adsorption sites, there are only small changes in the DOS due to the introduction of exact exchange. In particular, for the hollow site, we note that the peak corresponding to the $2\pi^*$ and 1π hybridization has the same intensity for HSE03 and PBE [panel (c)-CO]. Also the d_π intensity is almost the same as in the PBE case [panel (c)-CO, dashed line] as confirmed by the $2\pi^*$ occupation: it is 1.03 and 0.97 electrons using PBE and HSE03. *i.e.* it decreases by only 6 % using HSE03. Probably, the most pronounced difference between the $4d$ Rh and $5d$ Pt metal is the enhanced s occupation, related to the stronger binding of the $6s$ electrons (the shell structure requires that the orbitals are filled in the order $6s$, $4f$, $5d$,

6p placing the 6s electrons at significantly larger binding energies than 5s electrons). This effect is further enhanced by the HSE03 functional. As before, this should stabilize the CO in the hollow site due to the increased $\pi - s$ interaction. Indeed now the destabilization of the $\pi - d$ interaction in the hollow site is not sufficient to yield the top site as preferred adsorption site.

VI. DISCUSSION

Let us start with a brief discussion of the computational aspects of the current work. We have shown that periodic slab calculations using hybrid Hartree-Fock density functionals are perfectly feasible for metallic systems using a plane wave basis set. We have also shown that the HSE03 functional, suggested by Heyd, Scuseria and Ernzerhof, yields practically identical results as the more conventional PBE0 functional, albeit, at a computational cost that is reduced by almost a factor ten. This is achieved by replacing the long range part of the Fock-exchange by its density functional approximation, leading to a rapid k-point convergence of the non-local exchange and total energies. Thus the HSE03 functional presents a promising functional for large scale studies of molecules on surfaces.

Our study concentrated on the chemisorption of the CO molecule on *d*-metal surfaces, specifically Cu(111), Rh(111) and Pt(111). The study has been pursued using local and generalized gradient density functionals, and PBE0 and HSE03 hybrid Hartree-Fock density functionals. As expected, the LDA and GGA functionals give the wrong site preference for Cu, Rh and Pt. In contrast, the PBE0 and HSE03 functionals reduce this tendency, predicting the correct site order for CO on Cu(111) and Rh(111). In both cases, the fcc and hcp sites are destabilized by roughly 150 meV compared to the top site. Unfortunately the HSE03 and PBE0 functionals do not work so well for Pt(111), where the destabilization is only 50 meV for the fcc site and 80 meV for the hcp site, which is not sufficient to yield the correct site preference. In both Rh and Pt, we have made significant efforts applying for instance different PAW sets and parameters (not all have been discussed in detail) to make certain that the present numbers are essentially converged within the theoretical framework.

The wrong site order for Pt is not the only unsatisfactory aspect of our study; results for the energetics are also largely disappointing. It is well accepted that gradient corrected functionals have a tendency to overestimate adsorption energies on metal surfaces.^{2,77} One

would have hoped that admixing a certain fraction of the exact non-local exchange lifts this deficiency, but this hope is not fulfilled by the PBE0 and HSE03 functionals. In fact, Cu is the only case where the hybrid functionals improve the overall energetics. This is related to the upshift of the empty CO $2\pi^*$ orbital and a *simultaneous* downshift of the filled Cu $3d$ states, with both effects reducing, in concert, the $2\pi^* - d$ interaction; thus the top site becomes preferred.

For Rh and Pt, the d band is restrained to stay at the Fermi-level, and for the transition metals the main effect of the inclusion of non-local exchange is an increase of the d bandwidth. This increase of the d bandwidth counteracts the reduced interaction caused by the upshift of the CO $2\pi^*$ orbital. One therefore observes that the interaction energies generally increase from PBE, over HSE03 to PBE0, with the last one yielding the largest d band width and the largest CO-metal interaction energies. In a ball-pack, the increased metal bandwidth caused by the non-local exchange is the main origin of problems: it partially restores the CO $2\pi^* - d$ interaction that we had aimed to reduce by means of the hybrid functional. This counterbalance works efficiently for Pt, which has the largest d bandwidth and the largest interaction matrix elements between molecule and metal states.⁷⁸ We also qualitatively argued that further contributions in favor of restoring the back-donative interaction may come from an enhanced interaction of $2\pi^*$ states at the hollow site with *antisymmetric* combination of s metal states,⁶⁸ but our analysis is not able to quantify and separate s and d contributions.

Unfortunately, there are reasons to believe that the inclusion of a significant fraction of the non-local exchange and the concomitant increase of the d bandwidth in transition metals is the wrong physics. We have already commented on this issue in our recent work:³² the analogy between GW and hybrid functionals suggests that the amount of non-local exchange should be chosen system dependent, applying more Hartree-Fock like exchange in exchange dominated systems such as molecules and large gap insulators. In metals, on the other hand, the non-local exchange term in GW is almost entirely screened by the other electrons, so that the Coulomb hole term—corresponding to a local potential—becomes dominant. In metals, the proper description thus involves only a very weak screened-exchange interaction and the semi-local density functionals approximation should do a perfectly adequate job. The same conclusion is reached using the adiabatic connection fluctuation dissipation theorem (AC-FD).²⁴ In a forthcoming paper,⁷⁹ we will present results of hybrid-functional calculations

of CO adsorption extended to other systems representative of $4d$ and $5d$ metal surfaces, including the B3LYP functional. Unfortunately, also in this case, the results are generally discomfoting, suggesting that previous reports on the successful prediction of adsorption energies using B3LYP have to be considered with suspicion.

We are thus left with the intriguing problem, how to treat two disparate systems using the same unified theoretical footing. It is difficult to imagine that a hybrid functional with a fixed amount of non-local exchange is going to do the job. On passing, we also reiterate another result for hybrid functionals from Ref. 32: the exchange splitting in transition metals is significantly overestimated, resulting in too small atomization energies (found here as well for Pt) and a large overestimation of the magnetic moment in itinerant magnetic transition metals.

VII. CONCLUSIONS

We conclude that, although hybrid functional calculations for metals and metal surfaces are perfectly feasible, the results are by no means entirely satisfactory. The agreement with experiment is improved for CO on Cu(111), but the results are only marginally improved for CO on Rh(111) (correct site order but much too large adsorption energies) and hardly improved for CO on Pt(111) (wrong site order and too large adsorption energies). We have argued that this failure is related to the inclusion of non-local exchange in the metal slab which results in an incorrect description of the metal band width.

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TABLE I: Lattice constants a_0 (Å), bulk moduli B_0 (GPa), cohesive energies E_{coh} (eV) of bulk Cu, Rh and Pt obtained from LDA, GGA (PBE), PBE0 and HSE03 calculations. Results for HSE03 are based on calculations employing a 'reduced' $12 \times 12 \times 12$ k-point grid, those for LDA, GGA (PBE) and PBE0 a full $12 \times 12 \times 12$ grid, i.e. without downsampling (see text for details). Relative errors (%) with respect to experiment are shown in round brackets.

	a_0 (Å)	B_0 (GPa)	E_{coh} (eV)
Cu			
LDA	3.524 (−2.2 %)	184 (+29.0 %)	4.498 (+28.9 %)
PBE	3.635 (+0.9 %)	136 (−4.2 %)	3.484 (−0.2 %)
PBE0	3.636 (+0.9 %)	130 (−8.4 %)	3.046 (−12.7 %)
HSE03	3.640 (+1.0 %)	135 (−4.9 %)	3.066 (−12.1 %)
B3LYP (Ref.29)	3.700 (+2.7 %)	117 (−17.6 %)	2.892 (−17.1 %)
Exp	3.603	142	3.49
Rh			
LDA	3.752 (−1.2 %)	318 (+18.2 %)	7.382 (+28.4 %)
PBE	3.823 (+0.6 %)	254 (−5.6 %)	5.724 (−0.4 %)
PBE0	3.785 (−0.3 %)	291 (+8.2 %)	4.205 (−26.9 %)
HSE03	3.783 (−0.4 %)	305 (+13.4 %)	4.441 (−22.8 %)
Exp	3.798	269	5.75
Pt			
LDA	3.905 (−0.4 %)	306 (+10.0 %)	7.076 (+20.9 %)
PBE	3.965 (+1.2 %)	277 (−0.4 %)	5.668 (−3.1 %)
PBE0	3.932 (+0.3 %)	274 (−1.4 %)	4.648 (−20.5 %)
HSE03	3.932 (+0.3 %)	275 (−1.1 %)	4.900 (−16.2 %)
B3LYP (Ref.28)	4.05 (+3.3 %)	234 (−15.8%)	3.755 (−35.8 %)
Exp	3.920	278	5.85

TABLE II: Relevant equilibrium properties of the bare surfaces using the LDA, GGA (PBE), PBE0, and HSE03 functionals. d_{12} is the interlayer distance (in Å) between the first and second topmost layers. Numbers in round brackets refer to the change (in %) relative to the theoretical interlayer bulk distance ($a_0/\sqrt{3}$). E_{surf} is the average surface energy of the relaxed and unrelaxed side of the slab, normalized to the (111) surface unit cell. In this and the following tables, calculations for the 4 layer thick slab using $6 \times 6 \times 1$ (structural properties) and $8 \times 8 \times 1$ (energetics) k-point grids are reported. All calculations were performed using a $c(2 \times 4)$ surface unit cell.

	$d_{12}(\text{Å})$	$E_{surf}(\text{eV}/(111) \text{ unit cell})$
Cu		
LDA	2.01 (−0.9 %)	0.588
PBE	2.08 (−0.9 %)	0.455
PBE0	2.06 (−1.8 %)	0.465
HSE03	2.08 (−0.9 %)	0.453
B3LYP (Ref.29)	2.11 (−1.2%)	0.500
Rh		
LDA	2.13 (−1.6 %)	1.006
PBE	2.17 (−1.6 %)	0.814
PBE0	2.17 (−0.6 %)	0.849
HSE03	2.16 (−1.0 %)	0.845
Pt		
LDA	2.26 (+0.4 %)	0.813
PBE	2.30 (+0.7 %)	0.618
PBE0	2.30 (+1.3 %)	0.644
HSE03	2.30 (+1.3 %)	0.672
B3LYP (Ref.28)	2.39 (+2.1 %)	0.517

TABLE III: Relevant structural parameters and energetics of CO on the Cu(111) surface (top, fcc, and hcp sites) using the LDA, GGA (PBE), PBE0, and HSE03 functionals (all the distance in Å). d_{C-O} is the vertical distance between C and O, and in parenthesis the relative variation with respect to the theoretical value of the free CO molecule (%) is given; d_{C-X} is defined as the *minimum* height difference between the z coordinate of the C and metal atom directly involved in the C-X bonds; buckling b is the distance between the outermost and the innermost metal atom in the first layer; d_{12} is the mean change (%) of the distance between the first and second layer with respect to the theoretical value of the bare unrelaxed surface; E_{ads} is the adsorption energy in eV. The preferred site (and corresponding adsorption energy) is written in boldface.

Method	Site	d_{C-O} (Å)	d_{C-X} (Å)	b (Å)	d_{12} (%)	E_{ads} (eV)
Cu						
LDA	top	1.149 (+1.2%)	1.798	0.088	-1.0%	-1.286
	fcc	1.174 (+3.5%)	1.355	0.094	+0.5 %	- 1.660
	hcp	1.174 (+3.5%)	1.360	0.068	+0.4 %	-1.642
PBE	top	1.158 (+1.3 %)	1.844	0.124	-1.2 %	-0.709
	fcc	1.183 (+3.5 %)	1.395	0.109	+0.5 %	- 0.874
	hcp	1.182 (+3.4 %)	1.399	0.082	+0.6 %	-0.862
PBE0	top	1.144 (+0.9 %)	1.856	0.138	-1.7 %	- 0.606
	fcc	1.163 (+2.6 %)	1.425	0.135	+0.7 %	-0.579
	hcp	1.161 (+2.5 %)	1.450	0.105	+0.7 %	-0.565
HSE03	top	1.142 (+1.0 %)	1.864	0.146	-1.7 %	- 0.561
	fcc	1.160 (+2.6 %)	1.417	0.143	+0.7 %	-0.555
	hcp	1.158 (+2.4 %)	1.413	0.099	+1.2 %	-0.535

TABLE IV: Relevant structural parameters and energetics of CO on the Rh (111) surface (top, fcc, and hcp sites) using the LDA, GGA (PBE), PBE0, and HSE03 functionals. See caption III for details.

Method	Site	$d_{C-O}(\text{\AA})$	$d_{C-X}(\text{\AA})$	$b(\text{\AA})$	$d_{12}(\%)$	$E_{ads}(\text{eV})$
Rh						
LDA	top	1.155 (+1.8%)	1.810	0.167	+0.0%	-2.480
	fcc	1.185 (+4.5%)	1.350	0.083	+1.0%	-2.733
	hcp	1.187 (+4.6%)	1.330	0.083	+0.8%	-2.801
PBE	top	1.165 (+1.9 %)	1.827	0.213	+0.3 %	-1.870
	fcc	1.195 (+4.5 %)	1.379	0.082	+ 0.9 %	-1.906
	hcp	1.197 (+4.7 %)	1.348	0.096	+1.3 %	-1.969
PBE0	top	1.149 (+1.4 %)	1.834	0.234	+2.5 %	-2.109
	fcc	1.185 (+4.6 %)	1.330	0.048	+2.8 %	-2.024
	hcp	1.185 (+4.6 %)	1.344	0.118	+4.3 %	-2.104
HSE03	top	1.152 (+1.8 %)	1.811	0.172	+0.4%	-2.012
	fcc	1.193 (+5.5 %)	1.351	0.063	+1.9%	-1.913
	hcp	1.191 (+5.3 %)	1.342	0.100	+2.2%	-1.996

TABLE V: Relevant structural parameters and energetics of CO on the Pt (111) surface (top, fcc, and hcp sites) using the LDA, GGA (PBE), PBE0, and HSE03 functionals. See caption III for details.

Method	Site	$d_{C-O}(\text{\AA})$	$d_{C-X}(\text{\AA})$	$b(\text{\AA})$	$d_{12}(\%)$	$E_{ads}(\text{eV})$
Pt						
LDA	top	1.149 (+1.2%)	1.827	0.186	+0.5%	-2.251
	fcc	1.184 (+4.3%)	1.329	0.130	+2.5%	-2.601
	hcp	1.183(+4.2%)	1.314	0.132	+2.0%	-2.576
PBE	top	1.158 (+1.3 %)	1.839	0.227	+0.5 %	-1.659
	fcc	1.194 (+4.4 %)	1.329	0.132	+2.3 %	-1.816
	hcp	1.194 (+4.4 %)	1.324	0.149	+2.4 %	-1.750
PBE0	top	1.142 (+0.8 %)	1.818	0.237	+0.8 %	-1.941
	fcc	1.177 (+3.9 %)	1.304	0.215	+3.2 %	-1.997
	hcp	1.180 (+4.1 %)	1.291	0.226	+2.6 %	-1.944
HSE03	top	1.143 (+1.1 %)	1.821	0.200	+0.5 %	-1.793
	fcc	1.177 (+4.1 %)	1.320	0.177	+3.3 %	-1.862
	hcp	1.177 (+4.1 %)	1.330	0.177	+2.2%	-1.808

TABLE VI: Dependence of the site order on the sampling of the surface Brillouin zone using hybrid functionals and the PBE functional. Energies are referenced to the top site. PBE0 results are evaluated using the "full" k-point grid; HSE03 results are evaluated using the "reduced" as well as the "full" grid (numbers in round brackets) for the non-local exchange, see text for details.

	PBE0		HSE03		PBE	
	fcc	hcp	fcc	hcp	fcc	hcp
Cu						
$4 \times 4 \times 1$	0.095	0.097	0.099 (0.086)	0.106 (0.094)	-0.097	-0.089
$6 \times 6 \times 1$	-0.029	-0.004	-0.019 (-0.024)	0.010 (0.003)	-0.175	-0.158
$8 \times 8 \times 1$	0.027	0.041	0.006 (0.006)	0.026 (0.028)	-0.165	-0.153
Rh						
$4 \times 4 \times 1$	0.099	0.000	0.079 (0.081)	-0.006 (-0.022)	-0.040	-0.105
$6 \times 6 \times 1$	0.118	-0.007	0.076 (0.074)	0.005 (-0.003)	-0.067	-0.130
$8 \times 8 \times 1$	0.085	0.005	0.089 (0.094)	0.016 (0.048)	-0.061	-0.131
Pt						
$4 \times 4 \times 1$	0.047	-0.027	-0.091 (-0.112)	-0.045 (-0.062)	-0.127	-0.106
$6 \times 6 \times 1$	-0.073	0.067	-0.062 (-0.070)	-0.011 (-0.014)	-0.118	-0.094
$8 \times 8 \times 1$	-0.056	-0.003	-0.069 (-0.069)	-0.015 (-0.015)	-0.121	-0.095

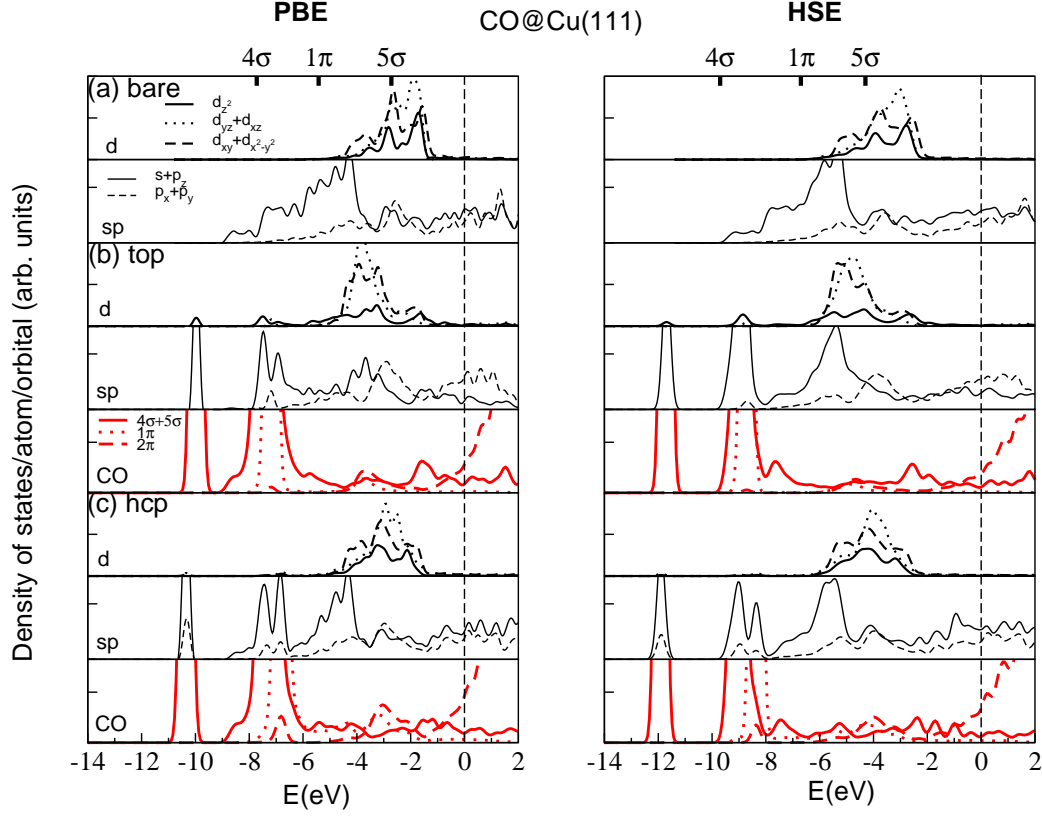


Fig. 1

FIG. 1: (Color online) Orbital resolved electronic densities of states (DOS) for the topmost Cu layer of the bare surface [panels (a)-d, (a)-sp] and for CO adsorbed at the top [panels (b)-d, (b)-sp, (b)-CO] and hcp hollow sites [panels (c)-d, (c)-sp, (c)-CO]. The DOS are projected onto the metal d states [panel (a)-d, (b)-d, (c)-d: continuous, dotted and dashed thick lines correspond to d_{z^2} , $d_{yz} + d_{xz}$ and $d_{xy} + d_{x^2-y^2}$ DOS respectively], onto metal sp states [panel (a)-sp, (b)-sp, (c)-sp: continuous, dashed thin lines correspond to $s + p_z$ and $p_x + p_y$ DOS respectively], and onto molecular orbitals [panel (b)-CO, (c)-CO: continuous, dotted and dashed thick red lines correspond to $4\sigma + 5\sigma$, 1π , $2\pi^*$ DOS respectively]. The Fermi level is located at 0 eV. In panel (a)-d, we show the one-electron energies of the 4σ , 1π , 5σ molecular levels aligned with the Fermi level using bold tick marks.

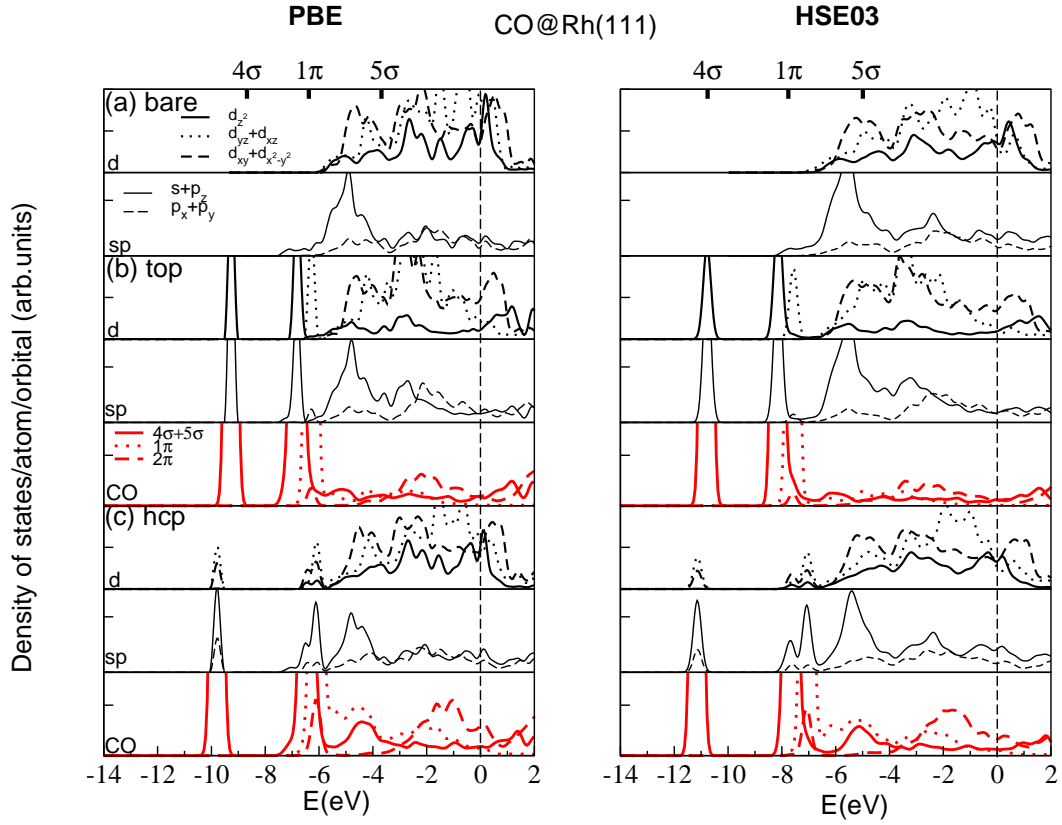


Fig. 2

FIG. 2: (Color online) Orbital resolved electronic density of states (DOS) for the topmost Rh layer of the bare surface (a) and for CO adsorbed at the (b) top and hcp (c) hollow site. See Caption of Fig. 1 for details.

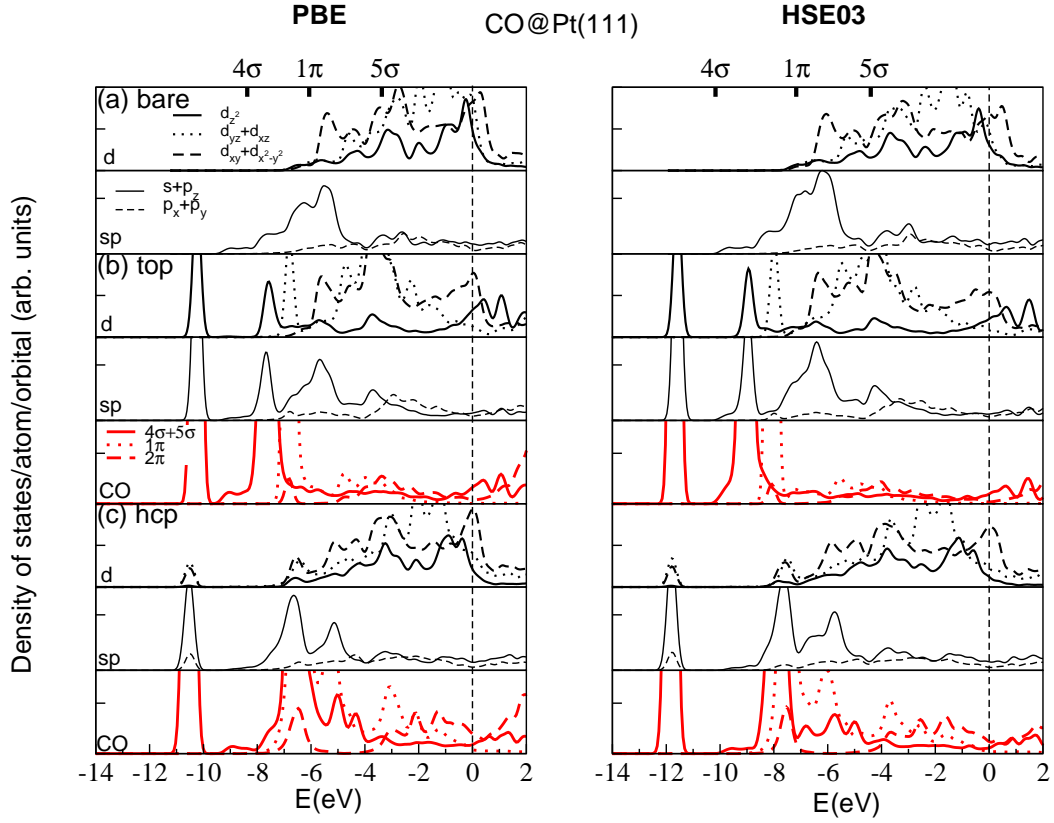


Fig. 3

FIG. 3: (Color online) Orbital resolved electronic density of states (DOS) for the topmost Pt layer of the bare surface (a) and for CO adsorbed at the (b) top and hcp (c) fcc site. See Caption of Fig. 1 for details.